Thus, structures deduced in concentrated solutions will reflect the effects of contiguous counterions. Enderby[25] has for example reported neutron scattering studies on concentrated aqueous nickel(II) chloride solutions and found that the angle between the nickel ion and the oxygen atom on the coordinated water molecules and the line bisecting the water protons decreases from 180° with concentration increase above about 0.1 mol dm^{-3}. The maximum angle of tilt from 180°, which he observed at 42 ± 8° for solutions in excess of about 1.0 mol dm^{-3}, is not, in our view, due to hydrogen bonding but the effect of the neighboring chloride ions. In his most concentrated solutions, around 4 mol dm^{-3}, the average separation between nickel and chloride ions is about 5 Å, and thus these ions are competing for the same water molecule in their solvation shells.

Acknowledgment. We thank the SERC for the provision of the Cary 14H spectrophotometer. The digitizing equipment was purchased on Harwell Contract EMR 1913. R.A.A. thanks the University of Leeds for a postgraduate research grant; T.R.G. thanks the University of Leeds and the Province of Alberta, Canada, for a travel grant under their Leeds-Alberta Link Scheme, and the Chemistry Department, University of Calgary, for hospitality and facilities during the preparation of this paper.

Registry No. $HgCl_3(MeOH)_2^-$, 132751-00-9; $HgBr_3(MeOH)^-$, 132751-01-0; $HgI_3(MeOH)^-$, 132751-02-1.

---

[25] Enderby, J. E. *Sci. Prog.* **1981**, *67*, 553.

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590,
Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396,
and General Electric Corporate Research and Development, Schenectady, New York 12301

Comparison of Isoelectronic Aluminum–Nitrogen and Silicon–Carbon Double Bonds Using Valence Bond Methods

Mary M. Lynam,[†] Leonard V. Interrante,[†] Charles H. Patterson,[‡,§] and Richard P. Messmer*,[∥]

Received January 16, 1990

In the reaction between trimethylaluminum and ammonia to form aluminum nitride, $(CH_3)_2AlNH_2$ is a postulated intermediate. Results of ab initio geometry optimization calculations for this species as well as H_2AlNH_2 and isoelectronic H_2SiCH_2 are presented. Each of these has a planar equilibrium skeleton with C_{2v} symmetry. Geometry optimizations were carried out by using generalized valence bond (GVB) wave functions. Al=N bond distances of 1.78 and 1.80 Å are predicted for the dihydro- and dimethylaluminum amides, respectively, which are slightly longer than the optimized Si=C bond distance of 1.74 Å in H_2SiCH_2. Al=N bond distances in these compounds are found to agree with a phenomenological correlation established by Haaland, which relates the ratio of covalent to dative character of such bonds to the observed bond distances. We compare the bonding in Al=N and Si=C molecules by analyzing the nature of the GVB orbitals describing the bonds and comparing their predicted dipole moments.

Introduction

Oligomeric alkylaluminum amides[1-9] $(R_2AlNR'R'')_n$ have recently been the subject of renewed interest owing to their potential utility as precursors to aluminum nitride[8,10,11] (AlN). As described in the review by Bahr,[12] E. Wiberg in 1939 elucidated a series of reactions involving the synthesis of methylaluminum amides and imides, which generate aluminum nitride when heated:

$$Me_3Al + NH_3 \rightarrow Me_3Al{\cdot}NH_3 \rightarrow (Me_2AlNH_2)_{2\,\mathrm{or}\,3} \rightarrow (MeAlNH)_n \rightarrow AlN \quad \mathrm{(I)}$$

The rational design of precursors to aluminum nitride requires a detailed knowledge of the intermediate steps that occur in the sequence of reactions in (I); in particular, in this work we are interested in the first methane loss step, which results in formation of aluminum amides. Interrante et al.[8] have studied the thermodynamic, kinetic, and mechanistic aspects of the reaction

$$Me_3Al + NH_3 \rightarrow Me_3Al{\cdot}NH_3 \rightarrow \tfrac{1}{3}(Me_2AlNH_2)_3 + CH_4 \quad \mathrm{(II)}$$

and have proposed monomeric Me_2AlNH_2 as an intermediate that participates as a catalyst in methane loss from the Lewis acid-base adduct $Me_3Al{\cdot}NH_3$.[9] This species may also be present as a gas phase or surface-adsorbed species in the chemical vapor deposition of AlN[13] and in solution during the thermal equilibration of the more thermodynamically stable trimeric species $(Me_2AlNH_2)_3$.[14] The theoretical studies reported here pursue the question of the structure and bonding in Me_2AlNH_2. We compare bonding and the predicted structure of Me_2AlNH_2 to those of two related molecules—H_2AlNH_2, and H_2SiCH_2.

The strong tendency of alkylaluminum amides to oligomerize results in formation of Lewis acid-base complexes of the type $(R_2AlNR'R'')_n$, whose structures consist of four- or six-membered aluminum-nitrogen rings whose size (n = 2 or 3) depends largely on the particular groups attached to Al or N. Heating the aluminum amides to moderate temperatures in solution results in elimination of alkane and formation of alkylaluminum imides $(RAlNR')_n$.[15-17] Imide aggregates with n up to 16 have been

---

[†] Rensselaer Polytechnic Institute.

[‡] University of Pennsylvania.

[§] Present address: Department of Pure and Applied Physics, University of Dublin, Trinity College, Dublin 2, Ireland.

[∥] General Electric Corporate Research and Development.

(1) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 287.
(2) McLaughlin, G. M.; Sim, G. A.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2197.
(3) Semenko, K. N.; Loblouski, E. B.; Dovsinskii, A. L. *J. Struct. Chem. (Engl. Transl.)* **1972**, *13*, 696.
(4) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metalloid Amides*; Ellis Horwood: Chichester, England, 1980.
(5) Amirkhalili, S.; Hitchcock, P. B.; Jenkins, A. D.; Nyathi, J.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 377.
(6) Interrante, L. V.; Carpenter, L. E.; Whitmarsh, C.; Lee, W.; Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 986.
(7) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1987**, *26*, 4341.
(8) Interrante, L. V.; Sigel, G. A.; Garbauskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252.
(9) Sauls, F. C.; Interrante, L. V.; Jiang, Z. *Inorg. Chem.* **1990**, *29*, 2989.
(10) Bolt, J. D.; Tebbe, F. N. Aluminum Nitride Fibers: Sintering and Microstructure. *Proc. Am. Ceram. Soc. Electron. Div.* **1987**, Oct 19.
(11) Tebbe, F. N.; Bolt, J. D.; Young R. J.; Van Buskirk, O. R.; Mahler, W.; Reddy, G. S.; Chowdry, U. Thermoplastic Organoaluminum Precursors of Aluminum Nitride. *Proc. Am. Ceram. Soc. Electron. Div.* **1987**, Oct 19.
(12) Bahr, G. In *Inorganic Chemistry, part II: FIAT Review of WWII German Science*; Klemm, W., Ed.; Dieterichsche Verlagsbuchhandlung: Wiesbaden, Germany, 1948; Vol. 24, p 155.
(13) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *132*, 472. Hanson, S. A.; Evans, J. F.; Boyd, D. C.; Gladfelter, W. L.; Ho, K. L.; Jesnen, K. V. Presentation at the 36th National American Society Meeting, Boston, MA, Oct 23-27, 1989; see Abstract No. TF-THM2.
(14) Sauls, F. C.; Czekaj, C. L.; Interrante, L. V. *Inorg. Chem.* **1990**, *29*, 4688.
(15) Wiberg, E.; May, A. *Z. Naturforsch.* **1955**, *B10*, 232.

reported[17] and structures are known for compounds where n = 4 units[16] and 6–8 units.[17]

A recent review of bonding in main-group elements[18] has collected a body of information on dative bonds. The data show that distances and strengths of dative bonds vary to a much larger degree than those of covalent bonds for a particular pair of atoms and that they have large inductive effects, especially at the acceptor atom. Aluminum–nitrogen bond lengths in the imide compounds above and in the oligomeric amides fall into the range 1.89–1.96 Å.[17] Recently, the synthesis and structure of the first aluminum–nitrogen compound with multiple Al–N bonds were reported.[19] This compound, $[\mathrm{MeAlN(2,6\text{-}\mathit{i}\text{-}Pr_2C_6H_3)}]_3$, is an $(\mathrm{AlN})_3$ analogue of borazine whose structure consists of a planar ring of alternating Al and N atoms with an average Al–N (multiple) bond distance of 1.78 Å and bond angles that deviate by ~5° from 120°. In our discussion we show that Al═N bond lengths of the amide compounds reported here fit into a correlation between covalent/dative character and bond length already established by Haaland.[18] We also make a comparison between the Al═N bond in H_2AlNH_2 and the Si═C bond in H_2SiCH_2. The Si═C bond in a number of compounds has been reviewed[20] and the conflict between electron diffraction data[21] and results of ab initio calculations[22] noted. X-ray crystallographic data[23a] for a compound with a bond distance of 1.702 Å and a microwave study[23b] of 1,1-dimethylsilaethylene are in agreement with the ab initio results and have resolved the conflict. The generally accepted Si═C bond distance in silaethylenes is now around 1.70 Å.

In this work we use a valence bond description of the electronic structure. As this approach is rather less familiar than the ubiquitous molecular orbital method, a few words regarding the valence bond approach used here may be in order.

Any many-electron wave function may be written as a resonating valence bond expansion; however, such a wave function is far too complex for routine calculations. Fortunately, in a great many cases, a single resonance structure provides a very good approximation to the electronic structure. In this case, if the spatial orbitals φ_i and the linear combination of spin eigenfunctions, Θ, are optimized, then one obtains the most general *independent particle model* description of the electronic structure. This wave function of eq 1 has come to be called the generalized valence

$$\Psi_{\mathrm{GVB}} = \mathcal{A}[\prod_i^N \varphi_i \Theta] \qquad (1)$$

bond (GVB)[24] wave function. Even this wave function is too complex to allow routine calculations (only a handful of such calculations have ever been done)! It is thus common to invoke two simplifying assumptions to permit calculations to be done. The first is the *perfect-pairing* assumption, which replaces the general spin function by one which assumes that pairs of orbitals are singlet-coupled; i.e., Θ is replaced by $\Theta_{\mathrm{PP}} = (\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$.... The second assumption is that the orbital pairs (e.g., the lone pairs, bond pairs, etc.) are mutually orthogonal, even though the orbitals within a pair may overlap; this is the *strong-orthogonality* approximation. There have been many calculations using the GVB method with the strong-orthogonality and perfect-pairing (SOPP) restrictions[25]

$$\Psi_{\mathrm{GVB\text{-}SOPP}} = \mathcal{A}[\prod_i^{N/2} (\varphi_{ia}\varphi_{ib})\Theta_{\mathrm{PP}}] \qquad (2)$$

where φ_{ia} and φ_{ib} are the singlet-coupled orbitals of the ith pair of electrons. We note two important properties of this wave function: (1) it is a generalization of Hartree–Fock theory and (2) the self-consistently determined orbitals of eq 2 are *unique*, unlike molecular orbitals. The restricted Hartree–Fock wave function is obtained by using the spin function $\Theta_{\mathrm{HF}} = \alpha\beta\alpha\beta\alpha\beta$... and by enforcing the restriction that $\varphi_{ia} = \varphi_{ib}$ for all pairs of spatial orbitals (i.e., for all values of index i). For the GVB wave functions, any change in the orbitals from the self-consistently determined wave function will *increase* the total energy of the system; hence they are *uniquely* determined. For the Hartree–Fock wave function, the form of eq 2 reduces to a single Slater determinant, and as a consequence, any unitary transformation of the self-consistently determined orbitals *will not change* the total energy. Thus the molecular orbitals of a Hartree–Fock calculation *are not uniquely determined*. Their shapes can be changed dramatically without affecting the energy.

Table I. Bond Distances and Angles for Me_2AlNH_2

bond	length, Å	angle	value, deg
Al–N	1.797	C–Al–N	119.4
Al–C	1.994	C–Al–C	121.2
N–H	1.026	H–N–H	110.3
C–H	1.096	H–Al–C	124.9

E = −367.83493 hartrees.

In this work, geometries of the three compounds mentioned above were optimized by using the form of the generalized valence bond wave function given in eq 2. However, in each case, only the six valence electron pairs were correlated that had the largest correlation effects. These correlated pairs are the two pairs in the Al═N or Si═C bonds and four bond pairs to the hydrogen atoms or methyl groups); the remaining valence electron pairs and core electrons were treated at the Hartree-Fock (HF) level and are written symbolically as {core}:

$$\Psi_{\mathrm{GVB\text{-}SOPP}} = \mathcal{A}[\{\mathrm{core}\}\prod_i^6 (\varphi_{ia}\varphi_{ib})\Theta_{\mathrm{PP}}] \qquad (3)$$

In the remainder of the paper, this approximate form of the GVB wave function will be used exclusively; for convenience, it will be referred to simply as the *GVB wave function*.

Results

A. Me_2AlNH_2. Two conceivable geometries for Me_2AlNH_2 are a planar structure with C_{2v} symmetry or a bent structure with C_s symmetry depending on whether an Al═N double bond *or* an Al—N single bond and a nonbonding lone pair are the most energetically favorable bonding situation. The optimized geometry obtained from the GVB calculation gave the planar double-bonded structure as the stable equilibrium geometry. The equilibrium bond distances and angles and the total energy are given in Table I, while the details of the basis sets used are given in the Appendix. In order to check the possibility of a local minimum for the Al-N

---

(16) del Piero, G.; Cesari, M.; Dozzi, G.; Mazzei, A. *J. Organomet. Chem.* **1977**, *129*, 281.

(17) (a) Cesari, M.; Perego, G.; del Piero, G.; Cucinella, S.; Cernia, E. *J. Organomet. Chem.* **1974**, *78*, 203. (b) Amirkhalili, S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1979**, 1206. (c) Cesari, M.; Cucinella, S. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. B., Eds.; Academic Press: London, 1987; Vol. 1, Chapter 6.

(18) Haaland, A. *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.

(19) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem.* **1988**, *100*, 1765; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699.

(20) Brook, A. G.; Bains, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(21) Mahaffy, P. G.; Gutowsky, R.; Montgomery, L. K. *J. Am. Chem. Soc.* **1980**, *102*, 2854.

(22) (a) Hanamura, M.; Nagase, S.; Morokuma, K. *Tetrahedron Lett.* **1981**, *22*, 1813. (b) Yoshioka, Y.; Goddard, J. D.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1981**, *103*, 2452. (c) Schaever, H. F., III. *Acc. Chem. Res.* **1982**, *15*, 283. (d) Gordon, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 4352. (e) Kohler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884. (f) Bell, T. N.; Kieran, A. F.; Perkins, K. A.; Perkins, P. G. *J. Phys. Chem.* **1984**, *88*, 1334. (g) Apeloig, Y.; Karni, M. *J. Chem. Soc., Chem. Commun.* **1984**, 768. (h) Luke, B. T.; Pople, J. A.; Krogh-Jespersen, M.; Apeloig, Y.; Karni, M.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 270. (i) Dobbs, K. D.; Hehre, W. J. *Organometallics* **1986**, *5*, 2057. (j) Colvin, M. E.; Kobayashi, J.; Bicerano, J.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *85*, 4563.

(23) (a) Wiberg, N.; Wagner, G.; Muller, G. *Angew. Chem.* **1985**, *97*, 220; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 229. (b) Gutowsky, H. S.; Chen, J.; Hajduk, P. J.; Keen, J. D.; Emilsson, T. *J. Am. Chem. Soc.* **1989**, *111*, 1901.

(24) Ladner, R. C.; Goddard, W. A., III. *J. Chem. Phys.* **1969**, *51*, 1073.

(25) (a) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1972**, *94*, 8293. (b) Hunt, W. J.; Hay, P. J.; Goddard, W. A., III. *J. Chem. Phys.* **1972**, *57*, 738. (c) Bobrowicz, F. W.; Goddard, W. A., III. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

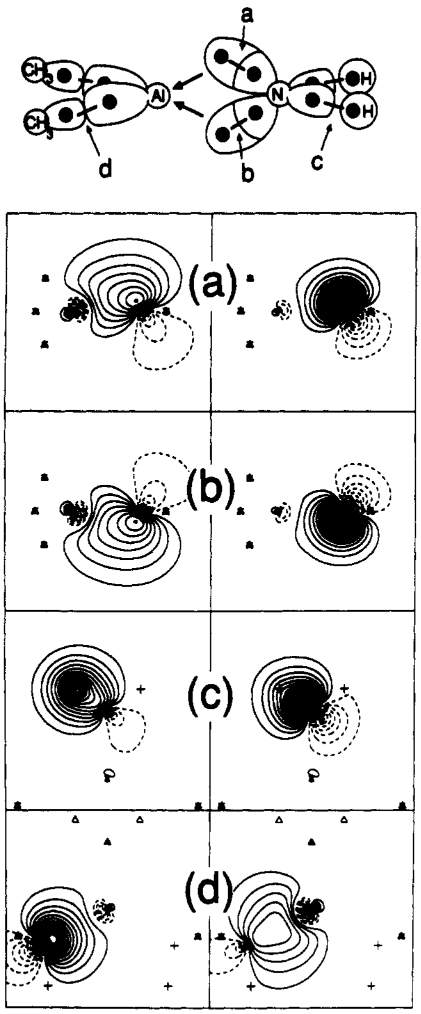

Figure 1. Contour plots of GVB orbitals for Me_2AlNH_2: (a, b) orbitals representing the Al=N bond perpendicular to the molecular plane; (c) orbitals representing the N—H bond; (d) orbitals representing the Al—C bond in the molecular plane. Contours are plotted at 0.04-au intervals in all figures.

single-bond structure, an appropriate starting geometry was assumed in which the Al–N bond distance was 1.95 Å and the bond angles about the nitrogen atom were 110°. This geometry yielded a total energy 10.16 kcal mol^{-1} ***higher*** than that of the equilibrium structure, and no local minimum in the total energy for a structure with C_s symmetry was found. In fact, calculations with assumed starting geometries rapidly collapsed to the planar structure described above. The Al–N equilibrium bond length of 1.80 Å (see Table I) is considerably shorter than the Al–N single-bond distances found in the oligomerized amide, which has an Al–N single-bond distance of 1.935 Å.[8]

A schematic representation of the bonding in the computed equilibrium structure of Me_2AlNH_2 is shown at the top of Figure 1. Contour plots of the self-consistent GVB orbitals for the aluminum–nitrogen bonds are shown in panels a and b of Figure 1. It can be seen that there is a double bond between the Al and N atoms and that these bonds are very polarized toward the nitrogen atom. The orbitals on the right side of panels a and b are clearly associated with the nitrogen atom, as the inner contours of highest probability amplitude are very near the N core. However, the inner contours of the orbitals at the left of the corresponding panels are not close to the Al core as they would be in a less polar bond, but are, in fact, rather close to the N core. The labels in the schematic diagram at the top correspond to the panels in which the contour plots are given. The lines connecting orbitals in the schematic show which orbitals are singlet-coupled. The polarization is so large that the bond may be described as two radially correlated pairs localized on the nitrogen atom forming dative bonds to the Al atom. However, starting from neutral fragments, Me_2Al and NH_2, one might expect one polar covalent bond between Al and N and one dative bond in which the N lone pair is accepted by the Al atom. But, of course, there are two ways of placing these bonds, and as a consequence a resonating valence bond wave function would be required for this description. The GVB wave function is based on a single resonance structure and as a consequence it gives a mean-field (average) description of these bonds: thus there are two equivalent bonds, both of which have polar covalent and dative character.

Table II. Bond Distances and Angles for H_2AlNH_2

bond	length, Å	angle	value, deg
Al–N	1.785	H–Al–N	118.5
Al–H	1.606	H–Al–H	123.1
N–H	1.026	H–N–H	110.3
		H–N–Al	124.8

$E = -298.77604$ hartrees.

Table III. Bond Distances and Angles for H_2SiCH_2

bond	length, Å	angle	value, deg
Si–C	1.740	H–Si–C	115.0
Si–H	1.495	H–Si–H	122.5
C–H	1.102	H–C–H	115.5
		H–C–Si	122.2

$E = -329.11634$ hartrees.

Panel c shows contour plots of the GVB orbitals that form one of the two equivalent N–H bonds; the left side is the orbital localized on the H atom and the right side in for that of the nitrogen atom. Panel d shows the contour plots of the GVB orbitals representing one of the two equivalent Al–C bonds; the orbital at the left is associated with the carbon atom and the orbital at the right is largely associated with the aluminum atom. The orbital plots in panels c and d are in the molecular plane. Note that the polar situation for the Al=N bonds, panels a and b, does not occur for the Al—C bond of panel d; i.e., the inner contour of the right orbital has its maximum amplitude near the Al atom. The predicted dipole moment is 0.9 D *with the negative pole toward Al.*

B. H_2AlNH_2. The equilibrium structures of dimethylaluminum amide and dihydroaluminum amide (Table II) are very similar. The Al=N bond distance is 0.01 Å shorter in the dihydrogen compound, and the N–H bonds are predicted to be the same length. Thus there are only minor substituent effects on the structure when the CH_3 groups are replaced by H atoms. Nonetheless, the contour plots of the GVB orbitals representing the Al=N, Al—H, and N—H bonds, which are shown in Figure 2, do appear to reflect these subtle changes. Panels a and b of Figure 2 again describe the Al=N double bond; however, in comparison to the corresponding orbitals of Figure 1, it can be noted that the innermost contour is missing in the orbitals at the left of Figure 2. This implies a very slight charge transfer from N to Al. The N–H bonds in the two molecules, Figures 1c and 2c, are essentially identical. However, there is a rather substantial difference in the Al orbital, i.e., the right orbital in Figures 1d and 2d, when it is bonded to a H atom as compared to a methyl group. In particular, the orbital is polarized toward the H atom as compared to the methyl group. This can be verified by noting that the innermost contour of this orbital in Figure 2 is much smaller and that the orbital has much greater amplitude outside the area between the two atomic cores. Both of these observations are consistent with the fact that the predicted dipole moment is increased to 1.3 D *with the negative pole toward Al.*

C. H_2SiCH_2. Silaethylene is unstable with respect to dimerization to disilacyclobutane. In an inert-gas matrix, the dimerization proceeds at temperatures above 10 K.[26] Theoretical predictions for the Si=C bond distance are in the range 1.692–1.728 Å in silaethylene[22a–e,g,i] and ~1.692 Å in 1,1-dimethylsilaethylene;[22b] electron-withdrawing substituents on the

---

(26) Maier, G.; Mihm, G.; Reisenauer, H. P. *Angew. Chem.* **1981**, *93*, 615.

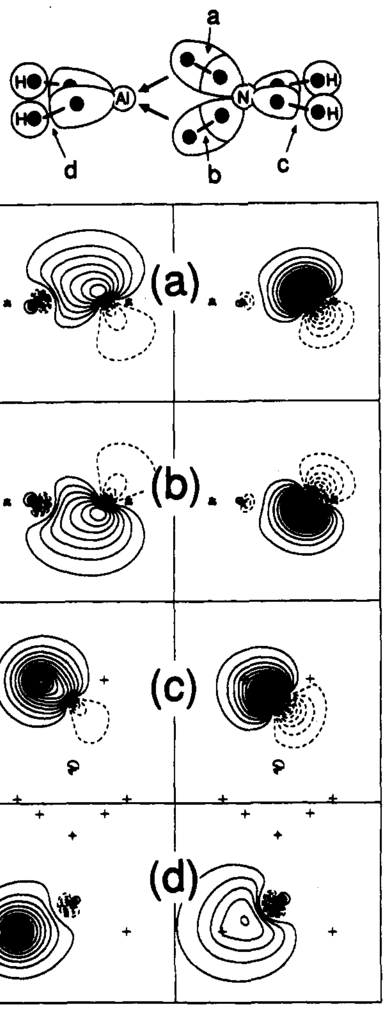

Figure 2. Contour plots of GVB orbitals for H_2AlNH_2: (a, b) orbitals representing the Al=N bond perpendicular to the molecular plane; (c) orbitals representing the N—H bond; (d) orbitals representing the Al—H bond in the molecular plane.

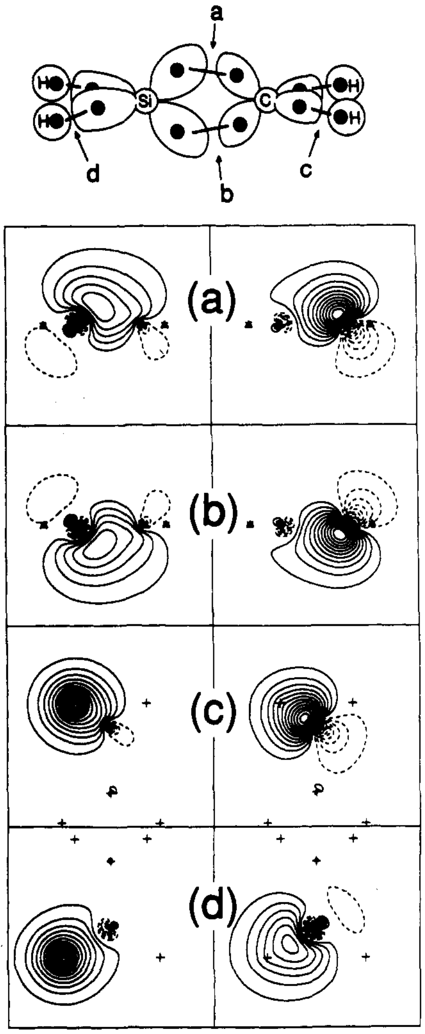

Figure 3. Contour plots of GVB orbitals for H_2SiCH_2: (a, b) orbitals representing the Si=C bond perpendicular to the molecular plane; (c) orbitals representing the C—H bond; (d) orbitals representing the Si—H bond in the molecular plane.

Si atom shorten the Si=C bond (by -0.034 Å for F[22d]), and the opposite effect is predicted for electron-withdrawing substituents on C (by +0.021 Å for F[22d]).

Our optimized geometry (Table III) for H_2SiCH_2 predicts an Si=C bond distance of 1.74 Å.[27] Contour plots of the GVB orbitals representing the Si=C bond in silaethylene are shown in panels a and b of Figure 3. As the schematic diagram at the top of Figure 3 suggests, the bonding between silicon and carbon is much more covalent than is the case for the Al=N double bond. This can be verified by analyzing the orbital plots: note how the left orbitals in panels a and b of Figure 3 have their innermost contour close to the Si core. This is in contrast to the corresponding Al orbitals of the Al=N double bond shown in panels a and b of Figures 1 and 2. The orbital contour plots describing the Si—H and C—H bonds are shown in Figure 3c,d. The predicted dipole moment is +0.6 D *with the negative pole toward C.*

Discussion

We may regard the Al—N double bond (for the molecules described above) as two equivalent bonds arising from an average of one dative bond and one polar covalent bond, whereas the Si=C bonds are composed of two polar covalent bonds. In order to understand more about the bonding in a compound such as Me_2AlNH_2, it is useful to make comparisons to other AlN compounds with a variety of bonding modes and to silaethylene. According to Haaland,[18] dative bonds have a much greater variation in length than covalent bonds and have strengths up to half the covalent bond strength. Electron-withdrawing groups bonded to the acceptor atom tend to shorten and strengthen dative bonds, while electron donors have the opposite effect. This is just the familiar inductive effect, but it is more pronounced in the case of dative bonds as compared to covalent bonds.[18]

A. Bond Distances. Dative bond distances in alane complexes with trimethylamine respond to groups with large inductive effects: the (purely dative) bond lengths in $Me_3N \rightarrow AlX_3$ are 1.96, 2.06, and 2.10 Å for X = Cl,[30] H,[31] and CH_3,[32] respectively. In a

---

(27) The Si=C bond length of 1.74 Å is without a d function on the carbon atom; when a d function on carbon is included the bond length decreases by less than 0.01 Å.

(28) Unlike the previous two cases discussed here, i.e., $(CH_3)_2AlNH_2$ and H_2AlNH_2, the H_2SiCH_2 molecule does not exhibit Ω-bonds (bent multiple bonds) as the lowest energy orbital configuration, using the GVB wave function with the SOPP restrictions. The σ,π-double-bond description is 0.105 eV lower in energy. However, we present the Ω-bond description here for two reasons: (1) it provides a more natural comparison with the bonding in the other molecules just discussed; (2) previous experience has shown that removal of the strong-orthogonality restrictions in the wave function always leads to an Ω-bond description (see ref 29).

(29) (a) Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543. (b) Schultz, P. A. Ph.D. Thesis, Department of Physics, University of Pennsylvania, 1988. (c) Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258.

(30) Grant, D. F.; Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr.* **1969**, *B25*, 377.

(31) Almenningen, A.; Gundersen, G.; Haugen, T.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3928.

(32) Andersen, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947.

compound, the "dative" and "covalent" character of a bond may be deduced empirically by starting from neutral fragments and constructing a single resonance structure consistent with the observed molecular structure. Then the extent of mixing is determined by considering the other canonical structures in which a particular bond is dative in one structure but covalent in an alternative one (e.g., as in a bridging NH_2 group). It has been noted that bonds with mixed covalent/dative character are shorter than pure dative bonds, and a correlation between bond length and the covalent/dative character of a series of compounds has been demonstrated.[18] For example, in the adducts just mentioned, the covalent/dative ratio (cov/dat) is 0/1 and a typical bond length (when no groups with large inductive effects are present) is 2.06 Å; in the trimeric amide $(Me_2AlNH_2)_3$, cov/dat is 1/1 and the bond length is 1.93 Å;[8] in the cage compound $(HAlN\text{-}i\text{-}Pr)_4$,[16] cov/dat is 2/1 and the bond length is 1.91 Å; in crystalline AlN,[33] cov/dat is 3/1 and the bond length is 1.88 Å.

These compounds all have single Al—N bonds, and the bond length decreases as the covalent/dative ratio increases. In the compounds studied in this work, the covalent/dative ratio is 1/1 but the Al=N bond order is formally 2. We should like to know the distances of single Al—N and double Al=N bonds for pure polar covalent bonds (i.e., *no* dative character). Haaland has regarded the bond between Al and the terminal NMe_2 groups in dimeric $(Me_2N)_3Al$ as being single, purely covalent bonds. This assumes a maximum of four bonds to an Al atom and that the nitrogen lone pairs on the terminal NMe_2 groups are not involved in the bonding. However, second-row elements bonded to electronegative elements are frequently hypervalent; i.e., there are more than four bonds to the hypervalent atom. This has recently been demonstrated explicitly in GVB calculations for sulfur dioxide and related molecules.[34] We expect, on the basis of these previous studies, that the Al to N bond involving the terminal NMe_2 groups is actually a double bond similar to the bond in H_2AlNH_2 or Me_2AlNH_2, which explains the similarities in Al=N bond distances: 1.81,[35] 1.78, and 1.80 Å, for $((Me_2N)_3Al)_2$, H_2AlNH_2, and Me_2AlNH_2, respectively. In agreement with this conclusion, a higher bond order (~2) than expected for $((Me_2N)_3Al)_2$ was reported recently on the basis of MO calculations.[36]

Thus we still require AlN reference distances for purely covalent single and double bonds. Lacking the appropriate experimental information for such bonds, we choose as a guide the Si—C (1.875 Å) and Si=C (1.702 Å) distances in $SiMe_4$[37] and $Me_2SiC(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$[23a] as experimental reference bond distances. The pure polar-covalent Si—C single bond is only slightly shorter than the predominantly polar covalent Al—N bond in crystalline AlN (1.88 Å).[33] The Al—N single bond in the trimeric amide $(Me_2AlNH_2)_3$, which experiences similar (methyl) inductive effects as the Si—C bond in $SiMe_4$, is not purely covalent but has a covalent/dative ratio of 1/1 and exhibits an (experimental) Al—N distance of 0.06 Å longer than the $SiMe_4$ reference single bond. Also, the monomeric amide (Me_2AlNH_2), with a covalent/dative ratio of 1/1, has a (calculated) bond distance 0.06 Å longer than the calculated double-bond reference distance in silaethylene (this work), which has no dative character. Thus, the correlation noted by Haaland,[18] that increased dative character results in longer bond lengths, appears to hold for the Al—N bonds, but a better set of reference compounds and a more extensive set of examples would be necessary to provide a definitive test of this correlation.

B. Substituent Inductive Effects. The electron-donating effect of methyl substituents on Al leads to a smaller dipole in Me_2AlNH_2 (0.9 D) compared to H_2AlNH_2 (1.3 D). This is also reflected in the shorter Al=N bond distance in H_2AlNH_2. As observed elsewhere,[34,42] substituent effects can be understood easily in a generalized valence bond framework by simple considerations of the orbitals. In a first-row element, the core size is very small and only allows four orbitals to form bonds. However, outside the first-row main-group elements, the cores are large enough to allow six (or more) polar covalent bonds to form. In the second row, for example, electron-withdrawing groups distort the orbitals to which they are bonded (away from the atom's core); this creates a partially unscreened core, which provides an additional attractive interaction sufficient to compensate the increased Pauli repulsions when the orbitals in other bonds move closer to the core. Overall, the effect is to shorten the other bonds to the atom that has the electron-withdrawing groups. The converse is found for electron-donating groups, which increase the Pauli repulsions between the bonds and result in increased bond lengths.

Conclusions

The bond lengths of $Y_2AlNY'_2$ compounds are likely to vary more significantly with substituents Y and Y′ than the corresponding cases of $Y_2SiCY'_2$ compounds. Also the Al=N bond strengths will be less than those of the corresponding Si=C bonds. Both of these features are predicted to arise as a consequence of the calculated substantial dative bond contribution to the Al=N bond and the observed correlation between dative bond character and bond strength and bond length.

Acknowledgment. This work was supported in part by grants from the Office of Naval Research and the Air Force Office of Scientific Research. We are grateful to Corinna Czekaj and Frederick Sauls for helpful discussions.

Appendix: Computational Details

GVB calculations within the strong orthogonality and perfect pairing (SOPP) approximations[38] were carried out by using the GVB2P5[39] and GAMESS[40] programs. The GAMESS program was employed for geometry optimizations. Polarized double-ζ (DZ) basis sets of Huzinaga[41] using the [11s7p/6s4p] contractions of Dunning[41] were used for aluminum and silicon atoms. The d polarization function exponents for Al and Si were 0.25 and 0.32; no polarization functions were employed on the C or N atoms in geometry optimizations. The Huzinaga valence DZ basis[41] sets (using the Dunning [9s5p/3s2p] contraction[41]) were used for carbon and nitrogen. The hydrogen atom basis set was the unscaled [3s/2s] contraction of the basis of Huzinaga.[41]

---

(33) Jeffrey, G. A.; Parry, Q. S.; Mozzi, R. L. *J. Chem. Phys.* **1956**, *25*, 1024.

(34) (a) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8059. (b) Patterson, C. H.; Messmer, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 4138.

(35) Ouzounis, K.; Riffel, H.; Hess, H.; Kohler, U.; Weidlein, J. *Z. Allorg. Allg. Chem.* **1983**, *504*, 67.

(36) Bryan, S. J.; Clegg, W.; Snaith, R.; Wade, K.; Wong, E. H. *J. Chem. Soc., Chem. Commun.* **1987**, 1223.

(37) Beagley, B.; Monaghan, J. J.; Hewitt, T. G. *J. Mol. Struct.* **1971**, *8*, 401.

(38) Hurley, A. C.; Lennard-Jones, J. E.; Pople, J. A. *Proc. R. Soc. London, A* **1953**, *220*, 446.

(39) Bair, R. A; Goddard, W. A., III; Voter, A. F.; Rappé, A. K. Yaffe, L. G.; Bobrowicz, F. W.; Wadt, W. R.; Hay, P. J.; Hunt, W. J. GVB2P5 program (unpublished); also ref 25.

(40) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, K.; Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(41) (a) Huzinaga, S. Approximate Atomic Functions II. Report from Department of Chemistry, The University of Alberta, Alberta, Canada, 1971. Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4.

(42) Messmer, R. P. *J. Am. Chem. Soc.* **1991**, *113*, 433.